Unprecedented participation of a four-coordinate hydrogen atom in the cubane core of lithium and sodium phenolates†

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Periodic trends in the chemical properties of elements are one of the most important and better established concepts in chemistry.† They are elegantly represented in the Periodic table, which provides a visual representation of the connection between atomic number, electronic structure and group relationships. One of the best examples of group trends is found for the alkali metals which exhibit well-defined changes in their atomic properties. However, the position of hydrogen as the first element of Group 1 is a question which is still open to debate. Undoubtedly, the similarity of the electronic structure of H (1s1) with that of the alkaline elements (ns1) is not, at least obviously, translated into a similarity in the properties of these elements (i.e. under ambient conditions the former is a diatomic gas and the latter are solid metals). In spite of this, over the years a close relationship between hydrogen and the light elements in the group (mainly Li) has been discerned in two respects. First, under extreme conditions, hydrogen can exhibit “metallic” properties typical of the alkali metals and, secondly, lithium has been attributed H-like characteristics. Thus, while hydrogen has been known for decades to participate in secondary interactions known as “hydrogen bonds” the analogous “lithium bond” was first suggested in 1958 and predicted theoretically by Kollman et al. in 1970. Since then the analogy has been generally accepted and “lithium bonds” have been the basis of many theoretical and spectroscopic investigations.† These similarities are not only important for a better understanding of fundamental chemical principles, but have also recently received attention in organocatalysis, after considering that hydrogen atoms can perform the role of Lewis acidic metal centres.

Given these similarities, as well as recent advances in synthetic methodology, and the plethora of organic and metal–organic crystal structure data available, an obvious question to ask is why have hydrogen and the alkali metals rarely, if ever, been observed to perform the same structural role in a molecular crystal structure?

One answer to this question lies in the difference in size which leads to very different structural preferences (Chart 1). Thus, the smaller H atom, when covalently bonded to an electronegative atom, has a strong preference for a nearly linear two-centre secondary interaction with another electronegative centre. Higher coordination numbers are possible via additional secondary interactions, although the occurrence of three-centre hydrogen bonds (bifurcated) is less common and four-centre (trifurcated) hydrogen bonds are rarely observed in organic crystals (Chart 1). By comparison, heavier Group 1 elements are larger atoms which can easily accommodate higher coordination numbers and they almost exclusively participate in three and four-centre interactions via either association (oligomers), coordination of neutral donor ligands (solvation) or commonly by a combination of both (Chart 1). As a result, one of the most common structural motifs for these elements is the solvated pseudocubane.

In order to induce a structural equivalence of H and the alkali metals, one approach might be using a ligand framework combining the preference for association into the pseudocubane structural motif with the ability to force H into a trifurcated bonding mode. Overcoming the fundamental structural differences in this way would provide the opportunity for H to participate in a molecular metallic array typical of the alkali metals (behaving as an alkali metal structurally). As part of our studies of metal complexes of...
high yield following protocols provided in the literature. Addition of one equivalent of an acidic enough phenol, such as pentachlorophenol (HOAr Cl), to acetonitrile solutions of \( \text{Li}_3 \) or \( \text{Na}_8 \) radicals of one compound, replacing one of the metallic positions, proving for the first time that a structural equivalence between these elements is indeed possible.

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the corner positions (Fig. 3), and therefore effectively replacing one of the metal positions of a typical Li/Na aryloxide cubane. To the best of our knowledge, the structures of complexes 5 and 6 prove for the first time that a hydrogen atom is capable of replacing an alkali metal atom in a typical alkali metal structural motif. In fact, by comparing the cores of complexes 3-6 (Fig. 3) it is clear that the Li/Na to H replacement does not impose significant modifications of the cubane motifs.

Spectroscopic data obtained from solutions of crystalline samples of complexes 5 and 6 are consistent with the retention of “monomeric” cubane structural motifs found in the solid state, and with the pseudo C₂-symmetry exhibited by the ligand framework (assuming free rotation for the OA⁺ group). Thus, the ¹H NMR spectrum of 5 exhibits only one resonance (δH = 0.89 ppm), while the ¹H NMR spectra of both complexes display just one set of signals for the aromatic protons of the equivalent phenolate rings, along with the expected AB multiplet for three equivalent methylene (NCH₂) groups. The retention of the N-H bond in solution is clearly supported by the appearance of quasi deshielded resonance [δH = 12.7 (S), 11.6 ppm (6)] values, which are even higher than that found for the free ligand 2, probably reflecting the existence of stronger NH···O₃ interactions in these metallated derivatives in solution.

In summary, we have reported for the first time the structural characterization of multi-metallated Group 1 derivatives of amine tris[phenolate] ligands, including the unprecedented participation of a metal-like hydrogen atom in the cubane core of an alkali metal (Li or Na) phenolate. We are now exploring the possibility of extending such a structural analogy to other related systems such as mixed-cubanes with different metals or anions.

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Notes and references

17. A preferential N–H deprotonation would be anticipated in view of the pKₐ values reported for related species [pKₐ ~ 9.80 (Me₃NH⁺)].
18. For 6 all the crystallizations yielded low-quality crystals which led to poor diffraction data. However, the crystallographic study allows for an unambiguous characterization of the structural motif.